Single-source precursors for α-Fe_2O_3 thin-films

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Introduction

Photoelectrochemical water-splitting is one method of producing hydrogen from non-hydrocarbon primary energy sources. Photoelectrochemical water-splitting is often performed using metal oxide thin-films[1], which ideally will have:

- A band-gap of suitable energy for efficient absorption of the solar spectrum
- A band-gap whose valence and conduction band energies bridge the redox potentials of the two relevant half-reactions:

$$4H^+ + 4e^- \rightleftharpoons 2H_2 \qquad E_{anodic} = 0.0\ V$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E_{cathodic} = 1.23\ V$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad E_{rxn} = -1.23\ V$$

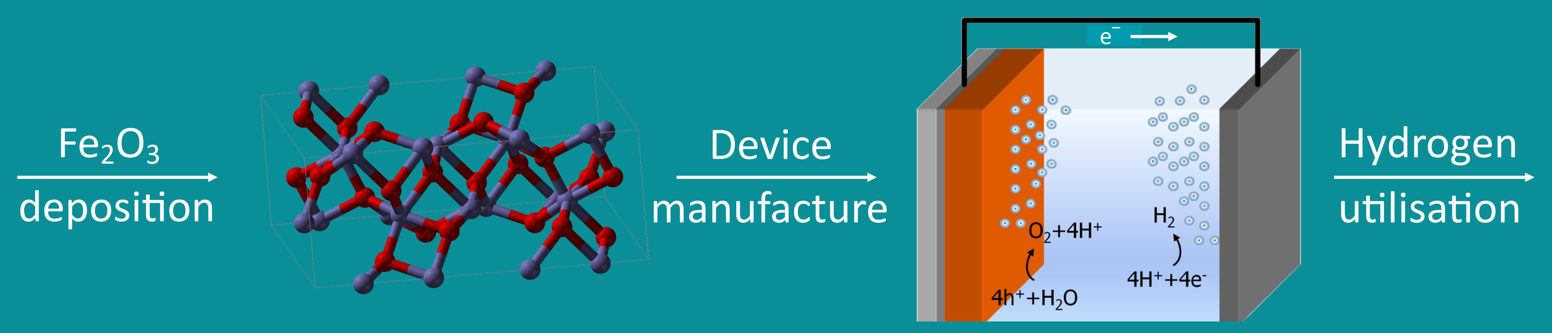


Fig. 1: Hydrogen-evolving devices can be manufactured from Fe_2O_3 precursors

Deposition of α-Fe_2O_3 thin-films

- α-Fe_2O_3 has a band-gap of 1.9–2.2 eV, making it a suitable photo absorber for water-splitting[2]
- Iron is earth-abundant and cheap, making hematite an inherently sustainable material.
- AA-CVD can be used to deposit a wide selection of single-source precursors.[3]

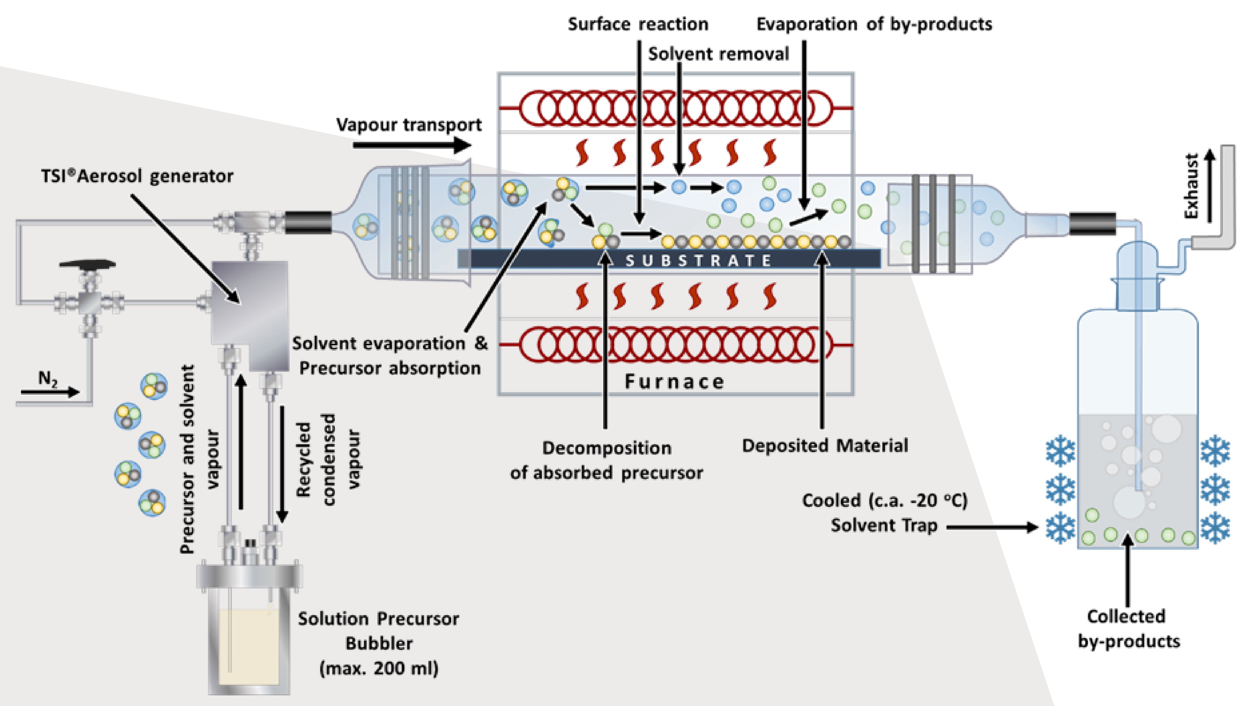
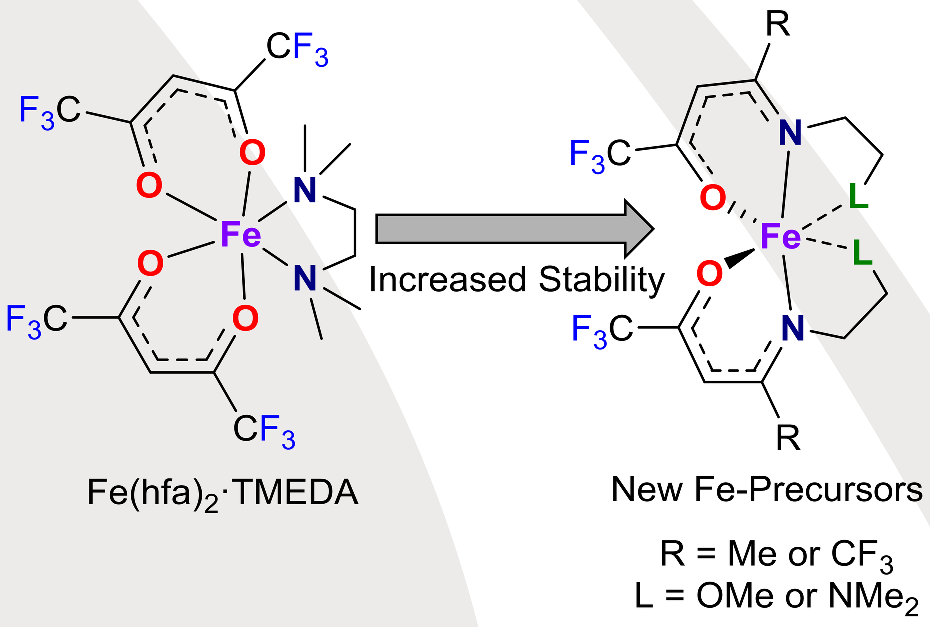


Fig. 2: Schematic of the aerosol-assisted chemical vapour deposition rig used

Precursor design

- The iron complex $Fe(hfa)_2 \cdot TMEDA$ has been shown to be a useful precursor for the deposition of α-Fe_2O_3.[4]
- At elevated temperatures the TMEDA ligand is labile, making the precursor in-volatile.
- By modifying the {fac} ligands to bear a pendant donor group we may be able to increase the stability of precursors.



Ligand synthesis

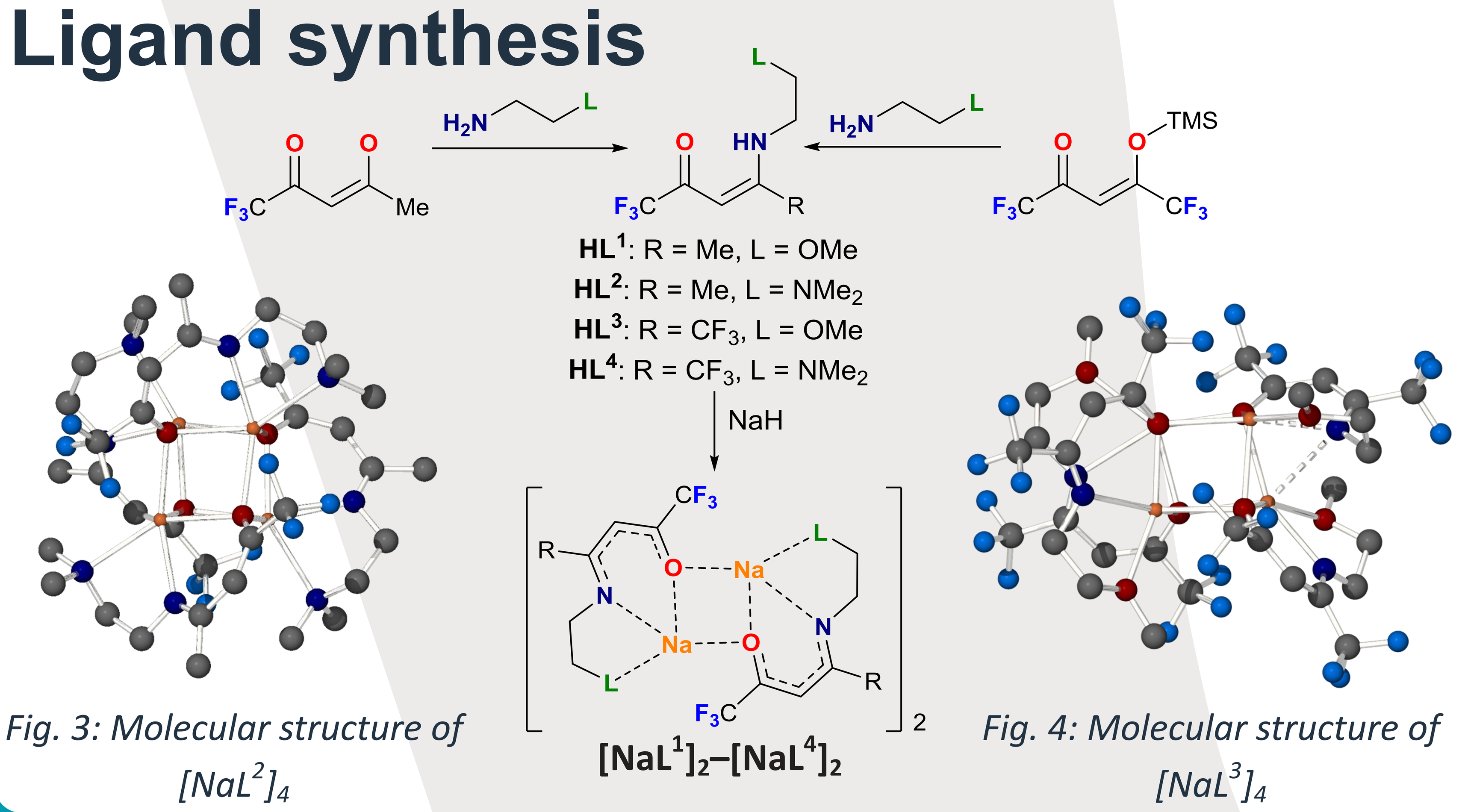


Fig. 3: Molecular structure of $[NaL^2]_4$

Fig. 4: Molecular structure of $[NaL^3]_4$

α-Fe_2O_3 single-source precursors

- A series of iron (II) complexes have been synthesised as prospective single-source precursors to α-Fe_2O_3.
- The molecular structure of several complexes have been determined by single crystal X-ray diffraction, and are shown below.

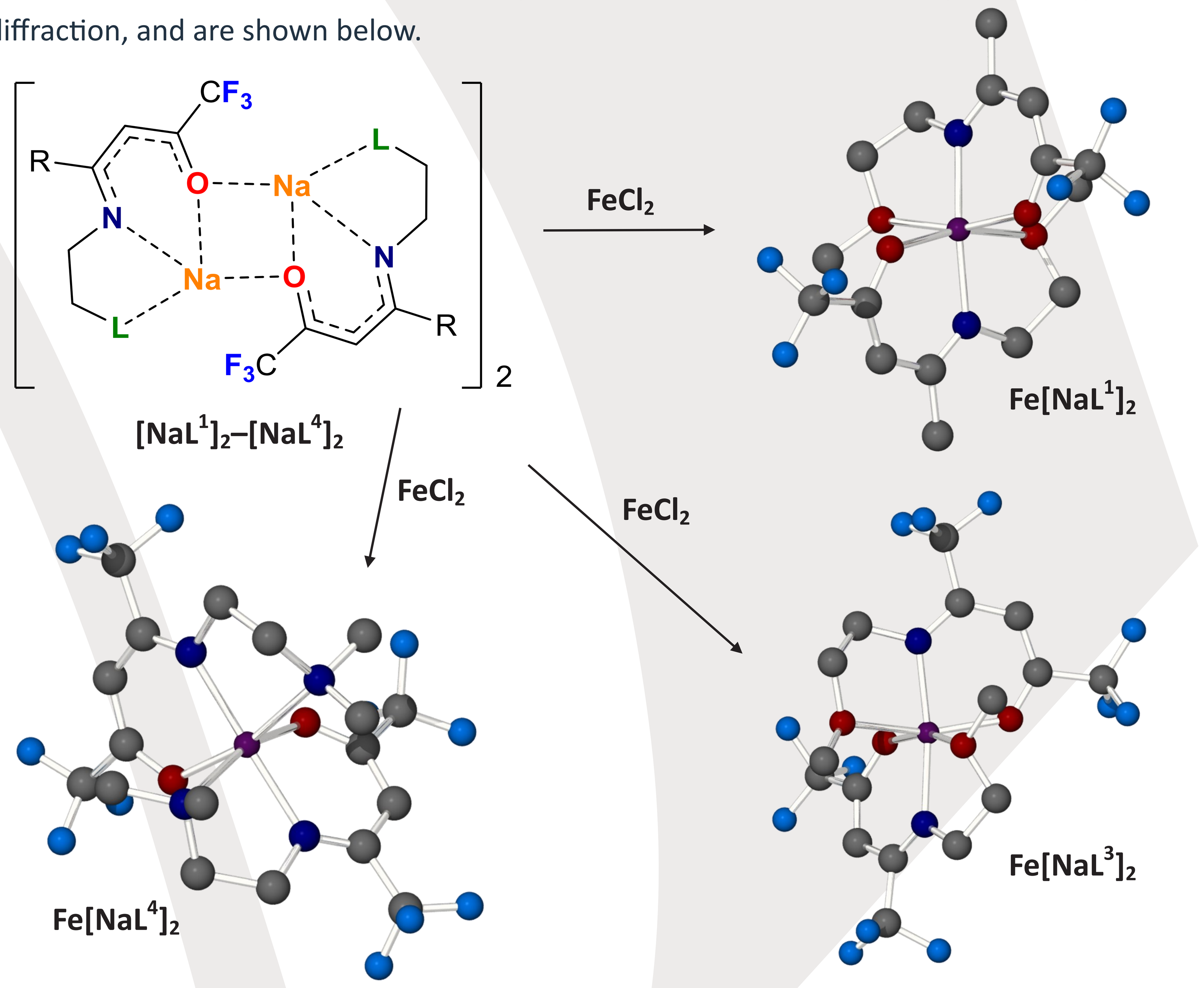
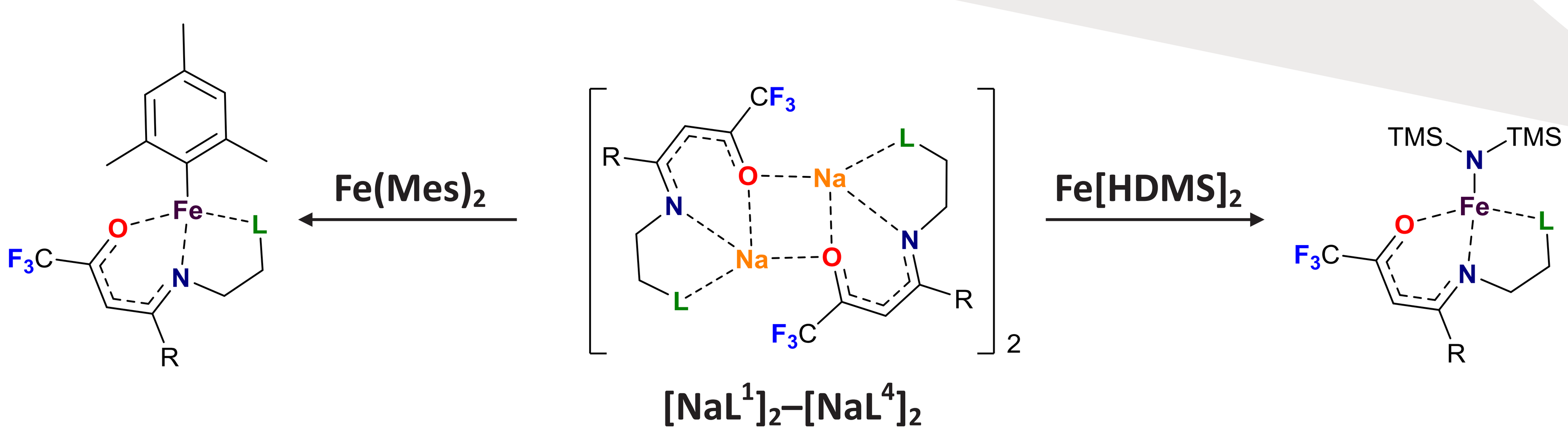


Fig. 5: Crystal structures of 3 iron (II) complexes (purple = iron, light blue = fluorine)

Future work

- A second series of mono-substituted iron (II) complexes will be synthesised using the ketoiminate ligands we have developed.



- Synthesised hematite precursors will be analysed using thermogravimetric analysis.
- Based on the decomposition observed by thermogravimetric analysis, lead precursors will be chosen for deposition by AA-CVD.
- Hematite thin-films will be produced and fully characterised.
- Devices will be manufactured and tested for photoelectrochemical water-splitting.

Conclusions

- A series of ketoiminate ligands and their sodium complexes have been synthesised and fully characterised.
- From the sodium salts, a series of potential single-source precursors for hematite have been synthesised and fully characterised.

References

[1] J. Chaoran, S. J. A. Moniz, A. Wang, T. Zhang and J. Tang, ***Chem. Soc. Rev.***, 2017, **46**, 4645–4660.

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[3] M. J. Powell, D. B. Potter, R. L. Wilson, J. A. Darr, I. P. Parkin and C. J. Carmalt, ***Mater. Des.***, 2017, 129, 116–124.

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